DETERMINATION OF IODINE IN ORGANIC MATERIALS

BY

ALDEN LA RUE CRITTENDEN

B. S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

DETERMINATION OF IODINE IN ORGANIC MATERIALS

Introduction

The pharmaceutical use of the dried, powdered thyroid glands of animals has become common. In the manufacture and use of such material, methods of analysis of the thyroid material for iodine content are of considerable importance and utility.

The most commonly used methods are those published in the various revisions of the United States Pharmacopoeia, particularly the eleventh and twelfth revisions.[6,7] There is, however, considerable dissatisfaction with these methods in the industries in which they are used. The methods are based on the work of a number of investigators,[1,2,3,4] some of whom are in complete disagreement in regard to proper procedures. Survey of the methods used shows a number of uncertainties and opportunities for objection.

Thyroid preparations consist very largely of protein matter. In the Pharmacopoeia procedures, this protein matter is destroyed by fusion of the sample with mixtures of alkalis in open crucibles. There is some possibility of loss of iodine from the open vessel in such methods. In the procedure described by the Pharmacopoeia, Revision XII, no oxidizing agent other than atmospheric oxygen is included in the mixture of alkalis, and, therefore, a great amount of unoxidized carbonaceous char results. Repeated washings of this char with hot water are necessary to insure that complete extraction of the iodine compounds has been obtained.

According to Pharmacopoeia methods, the iodine compounds extracted from the organic matter are converted into iodates by oxidation with chlorine water or bromine water. The iodate resulting from the oxidation is treated with excess potassium iodide and the liberated iodine

titrated with standard sodium thiosulfate solution. Some bromates or chlorates may be formed in the oxidation process, and these are difficult to remove. The presence of these compounds may give erroneous results unless great care is taken to obtain conditions under which iodate, but not bromate or chlorate, is reduced by the iodide.

The development of a new procedure which would avoid the above mentioned difficulties was undertaken.

Experimental

The destruction of protein matter by the use of fusion with sodium peroxide in a closed Parr bomb was investigated. It was found that thyroid materials can be quickly and conveniently oxidized under these conditions. No loss of iodine was found to occur, and methods for the avoidance of interference by peroxides were found.

Nitrites were found to be formed by the action of sodium peroxide upon proteins. These nitrites were found to interfere in the subsequent analysis because of their reducing action toward iodates.

Difficulty was experienced because of the occasional formation of finely divided carbon in fusions of proteins with sodium peroxide. The alkaline fusion mixtures were dissolved in water and the solutions treated with excess bromate before acidification. The bromate was found to be effective in oxidizing nitrites, peroxides, and the troublesome carbonaceous matter, thereby removing interferences by these substances.

The use of bromine water in weakly acid solution for the oxidation of iodine compounds to iodates was found to be quantitative over the pH range from 2.5 to 4.0. The excess reagent could be removed easily by treatment with aqueous phenol. Chlorine water was found to be less satisfactory and the excess more difficult to remove.

Interferences by bromates and chlorates were avoided by reducing these compounds to halides by treatment with sodium sulfite in strongly acid solution.

Proposed Procedure

The following procedure for the analysis of thyroid materials for iodine content is proposed. A 0.5 gram sample is mixed with 15 grams of sodium peroxide. One gram of potassium perchlorate and 0.2 gram of sucrose are added as accelerators. The bomb is closed and heated to the point of fusion of the peroxide. The bomb is then cooled, opened, and the contents dissolved by placing the bomb in 70 ml. of water, warming, if needed, to start the decomposition. Peroxides are decomposed by boiling the solution for five minutes. The alkaline solution containing the iodine is filtered through a Whatman No. 50 filter paper into a receiver containing 5 ml. of 1.0 normal potassium bromate-potassium bromide solution. The bomb is washed twice with 4 normal sulfuric acid, adding the washings to the main solution.

The filtrate is acidified with 25 ml. of 18 normal sulfuric acid. The free bromine formed by the action of bromate on bromide is reduced by dropwise additions of sodium sulfite solution. The solution is heated to boiling to accelerate this reduction, adding more sulfite as needed to reduce the bromine formed. An excess of a few drops of sulfite is maintained.

The solution is cooled, neutralized with sodium hydroxide, and acidified to the methyl orange end point with hydrochloric acid. Five ml. of 45 per cent primary sodium phosphate solution is added to provide a buffer action, and saturated bromine water is added dropwise until a few drops excess is present, as shown by the yellow color. The bromine oxidizes iodine compounds to iodates, oxidizes the excess sulfite to sulfate, and bleaches the indicator color. After five minutes standing, 1 ml. of saturated aqueous phenol is

added; the excess bromine is then removed by bromination of the phenol. This process is slightly slow. After allowing five minutes for the removal of excess bromine, excess potassium iodide (3 grams) is added, together with 3 ml. of 6 normal hydrochloric acid. The liberated iodine is titrated with standard 0.01 normal sodium thiosulfate solution, adding starch solution as the indicator near the end point.

The proposed procedure was checked by analyses of mixtures of casein and diiodotyrosine. These mixtures were prepared by mixing weighed quantities of the dried reagents in a ball mill. The diiodotyrosine was analyzed for iodine content by the method of Lemp and Broderson.[5] The theoretical iodine contents of the mixtures were calculated.

Results obtained by the proposed method with two casein-diiodotyrosine mixtures agreed with the theoretical value within experimental error. The average deviation of results from the correct result was found to be plus or minus 0.5 per cent of the total iodine present. The amounts of iodine present were about the same as the quantities of iodine found in thyroid materials, being between 0.17 and 0.24 per cent iodine.

Results obtained by the current United States Pharmacopoeia method were found to be slightly low, as previously reported by other workers.[4]

Results obtained by the proposed procedure with actual thyroid materials agreed fairly well with results obtained by the methods specified in the Pharmacopoeia, the more accurate results by the proposed method being a little higher.

The proposed procedure was found to require considerably less time for completion than do the Pharmacopoeia methods.

Bromate was shown to be formed in the course of analysis by the method used in the United States Pharmacopoeia, Revision XII.[7] It was further shown that this bromate was responsible for error in results obtained by this method.

The use of the Parr bomb for thyroid analysis was shown to be completely satisfactory and not hazardous.

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VITA

The author was born November 27, 1920, in Wichita, Kansas, and received his primary and secondary education there. After graduation from high school in 1938, he entered the Municipal University of Wichita, attending there until 1940. He then transferred to the University of Illinois, receiving the Bachelor of Science degree in 1942. He then entered the Graduate School of the University of Illinois and held a teaching assistantship in the Analytical Division of the Department of Chemistry. He resigned this appointment in 1944 in order to enter the Naval service, being reappointed to the position upon his release from service in 1946.

The author is a member of the American Chemical Society, Sigma Xi, and Phi Lambda Upsilon.